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(54) Polyester containing 2-methyl-1,3-propylene terephthalate units

(57) A polyester resin which comprises terephthalic acid units, tetramethylene glycol units and 2-methyl-1,3-propanediol units, the 2-

methyl-1,3-propanediol units being contained in an amount of from 0.1 percent by weight, as 2-methyl-1,3-propanediol terephthalate, based on the whole weight of the polyester, to 99 mol percent, based on the total weight of the diol component.

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## SPECIFICATION

## Polyester containing 2-methyl-1,3-propylene terephthalate units

5 The present invention relates to polyester resin which comprises as one component 2-methyl-1,3-propylene terephthalate units, in particular to a polyester copolymer or polyester blend which comprises tetramethylene terephthalate units and 2-methyl-1,3-propylene terephthalate units. 5

The polyester resin or blend according to the invention may be obtained from (A) terephthalic acid, (B) 2-methyl-1,3-propanediol and (C) tetramethylene glycol. The polyester copolymer of the invention comprises monomer units (A), (B) and (C) as the essential components. The polyester blend of the invention may comprise a polyester of monomers (A) and (C) and another polyester of monomers (A) and (B). The blend may also comprise a polyester of monomers (A), (B) and (C) with the polyester of monomers (A) and (C) and/or the polyester of monomers (A) and (B). One purpose of the invention is modification of polytetramethylene terephthalate by the incorporation of 2-methyl-1,3-propylene terephthalate units. 10

Heretofore, many commercial polyester resins contain the glycol component such as for example ethylene glycol as in polyethylene terephthalate and tetramethylene glycol as in polytetramethylene terephthalate. These glycols have two primary hydroxyl groups. This is due to the fact that primary hydroxyl groups are very reactive and easily form ester bonds. 15

Polytetramethylene terephthalate (hereinafter referred to as "PBT") resin is a thermoplastic polyester resin having a high crystallizability, and it has a good compatibility with various fillers and additives. A reinforced PBT resin having, for example, glass fibre, mica, talc or flame retardant incorporated therein shows excellent characteristics when used in various fields. Therefore, it is widely used for example as electric and electronic parts and automobile parts in various industries. More specifically, the PBT resin has excellent mechanical strength, durability, weatherability, chemical resistance, heat resistance, dimensional stability and electrical properties. Furthermore, the PBT resin has a higher crystallinity than that of a polyethylene terephthalate resin. Moreover, the PBT resin has a high crystallization speed and hence, the cooling solidification speed of the PBT resin is high. Still further, the PBT resin has a good flowability. Accordingly, the PBT resin is excellent from the point of view of being shaped. The PBT resin having the above-mentioned characteristics is an excellent engineering plastic material in which electric and mechanical characteristics are well-balanced with the processing characteristics. 20 25 30

However, the PBT resin also has defects as described below.

(1) The PBT resin is naturally inferior in the dimension precision to amorphous and hardly crystallizable plastics, and it is easily influenced by the mold temperature distribution. Moreover, the moulding shrinkage depends greatly on the thickness, and because of this property and the deviation of the cooling speed, deformation or sinking is readily caused. In PBT resin reinforced for example by a glass fibre this undesirable property promotes shrinkage anisotropy due to the orientation of the fibre, and deformation is readily caused and so-called warps are formed. 35

(2) The PBT resin which is not especially reinforced is poor from the point of view of flexibility and has a high notch sensitivity.

Means for moderating the foregoing defects which are known are a method in which the crystallizability is reduced by substituting part of terephthalic acid with an aliphatic dicarboxylic acid or blending other resin into the PBT resin to reduce deformation due to shrinkage in the moulding step, and a method in which a filler is incorporated having a lower anisotropy than glass fibre, such as glass bead, talc or mica. However the resins obtained according to these methods are not satisfactory from the point of view of deformation of a moulded PBT article, large contraction, low resistance to impact and high notch sensitivity. 40 45

The 2-methyl-1,3-propanediol used in this invention also has two primary hydroxyl groups, and has almost the same reactivity as tetramethylene glycol. When reacted together with ethylene glycol or tetramethylene glycol and with terephthalic acid, it yields easily a polyester copolymer containing 2-methyl-1,3-propylene terephthalate at an arbitrary ratio. 50

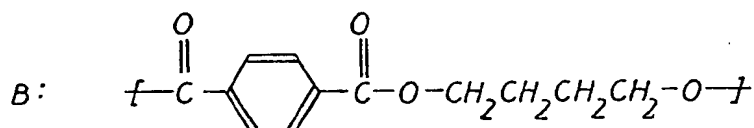
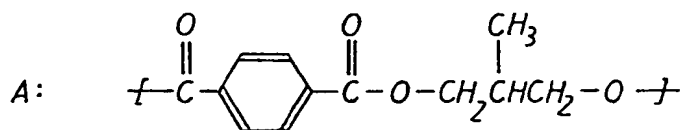
The 2-methyl-1,3-propanediol is a structurally asymmetrical glycol along the main chain, having one methyl group as the side chain. Therefore, a polyester copolymer containing this diol as one component is irregular in structure and low in crystallinity. We have found that this can lead to improvement of moulding shrinkage and flexibility.

55 In the polyester resin according to the invention, the 2-methyl-1,3-propanediol units are contained in an amount of from 0.1 percent by weight, as 2-methyl-1,3-propanediol terephthalate based on the whole weight of said polyester, to 99 mol percent, based on the total weight of the diol component. 55

The present invention relates preferably to a polyester copolymer which comprises terephthalic acid as the acid component and 1 to 99 mol% of 2-methyl-1,3-propanediol and 99 to 1 mol% of tetramethylene glycol as the glycol component. The glycol component is preferably composed of 5 to 95 mol% of 2-methyl-1,3-propanediol and 95 to 5 mol% of tetramethylene glycol. If the content of 2-methyl-1,3-propanediol is less than 1 mol%, the resulting copolymer will not be improved in moulding shrinkage and flexibility. On the other hand, if the content of 2-methyl-1,3-propanediol is more than 99 60

mol% the resulting copolymer tends to have a lower melting point, increased transparency because of lowered crystallinity, and poorer thermal and mechanical properties. Thus, the resulting copolymer has limited applications.

The polyester copolymer in this invention has irregularly distributed repeating units represented by the following formulae A and B, A being 1 to 99 mol% and B being 99 to 1 mol%.



The best mode of the polyester according to the invention is a copolymer having a B component content of 0.1 to 25 preferably 1 to 20 percent by weight based on the whole weight of the polyester.

We have made further studies to obtain an improved polyester resin composed substantially or a PBT resin without the above discussed defects and found that when a poly-2-methyl-1,3-propylene terephthalate component consisting of terephthalic acid and 2-methyl-1,3-propanediol is incorporated in an appropriate amount into a PBT resin, the percent shrinkage is remarkably reduced and the flexibility is highly improved while the mechanical and electrical characteristics are maintained at practically applicable levels.

More specifically, in accordance with the present invention, there is provided a modified polyester resin composition comprising a polytetramethylene terephthalate resin composed of terephthalic acid and tetramethylene glycol and 0.1 to 25% by weight, based on the polyester resin, of a poly-2-methyl-1,3-propylene terephthalate component composed of terephthalic acid and 2-methyl-1,3-propanediol.

The above-mentioned polyester copolymer may be produced for example by conventional processes for producing polyesters. That is, it can be produced by a process in which a dicarboxylic acid and a diol are polycondensed directly, or by a process in which a lower alkyl (e.g. methyl or ethyl) ester or halogen derivative or dicarboxylic acid is reacted with a diol.

The polycondensation process involving so-called ester interchange using a lower alkyl (e.g. methyl or ethyl) ester of carboxylic acid is exemplified as follows:— dimethyl terephthalate and an excess of mixed diols of tetramethylene glycol and 2-methyl-1,3-propanediol, the total being 1.1 to 2.0 times the molarity of dimethyl terephthalate, are subjected to an ester interchange reaction under a nitrogen stream at 150 to 240°C under normal atmosphere pressure, using a common esterification catalyst. During the reaction, methanol is distilled off. A catalyst and colour protectant are added, as required. Polycondensation is performed at about 200 to 280°C under a reduced pressure lower than 5 mm Hg. The above-mentioned catalyst is exemplified by titanium compounds e.g. tetramethoxytitanium, tetraethoxytitanium, tetra-n-propoxytitanium, tetra-iso-propoxytitanium, and tetrabutoxytitanium; tin compounds e.g. di-n-butyltin dilaurate, di-n-butyltin oxide, or dibutyltin diacetate; acetates of magnesium, calcium or zinc; or antimony oxide. Mixtures of catalysts may be used, for example, two or more of the titanium compounds or a mixture of magnesium acetate and antimony oxide. These catalysts are preferably used in an amount from 0.002 to 0.8 wt% based on the total copolymer to be produced. Effective colour protectants are phosphorus-containing compounds such as for example phosphorus acid, trimethylphosphite, tridecyl phosphite, triphenyl phosphite, trimethyl phosphate, tridecyl phosphate and triphenyl phosphate. They are preferably used in an amount from 0.001 to 0.3 weight % based on the total copolymer produced. In addition to the colour protectant, other additives such as for example polymerization accelerators, brightening agents, and light stabilizers may be used.

The polyester copolymer of this invention may be produced from terephthalic acid and 2-methyl-1,3-propanediol and/or tetramethylene glycol as the starting materials. It may contain as copolymer components polybasic aliphatic carboxylic acids such as for example, adipic acid, azelaic acid, or sebacic acid, polybasic aromatic carboxylic acid such as for example isophthalic acid, trimellitic acid, pyromellitic acid, or 2,6-naphthalene-dicarboxylic acid; and polyhydric alcohols such as for example ethylene glycol, propylene glycol, neopentyl glycol, 1,6-hexanediol, 1,4-cyclohexanediol, cyclohexanedimethanol, trimethylolpropane, or pentaerythritol.

The modified polyester resin composition of the present invention can be obtained according to optional methods by for example blending (1) a resin composition composed substantially of a PBT

resin with (2) a resin composition composed substantially of a polyester formed by polymerizing terephthalic acid with 2-methyl-1,3-propanediol and/or (3) a resin composition composed substantially of a copolyester obtained by polymerizing terephthalic acid with tetramethylene glycol and 2-methyl-1,3-propanediol.

- 5 Blending can be accomplished for example by using customary methods and apparatus, for example, a chemical method in which the polyesters are blended while dissolved in a solvent or a mechanical method in which the polyesters are kneaded for example by a roll mixer, a Banbury mixer, an extruder or a moulding machine. 5

- 10 The above-mentioned polyesters and copolyesters (1), (2) and (3) may be prepared in the same way as mentioned above in respect of the copolymer. The polyesters and copolyesters (1), (2) and (3) may include other monomers as mentioned above. 10

- 15 The poly-2-methyl-1,3-propylene terephthalate component composed of terephthalic acid and 2-methyl-1,3-propanediol, which is contained in the modified polyester resin composition of the present invention, is incorporated in an amount of 0.1 to 25% by weight, preferably 1 to 20% by weight, based on the polytetramethylene terephthalate component composed of terephthalic acid and tetramethylene glycol. If the amount of the poly-2-methyl-1,3-propylene terephthalate component is smaller than 0.1% by weight, substantial reduction of the moulding shrinkage or substantial improvement of the flexibility cannot be expected. If the amount of the above component is larger than 25% by weight, the melting point and crystallinity of the resulting resin composition are extraordinarily lowered, and the thermal and mechanical strength characteristics are considerably reduced. 15 20

The copolymers obtained according to the present invention are useful as moulding materials and adhesives.

The invention is illustrated by the following non-limitative examples, in which "parts" means "parts by weight". The values in the Tables were measured as follows:

- 25 (1) Content of poly-2-methyl-1,3-propylene terephthalate 25  
The content shown in Tables 1 and 2 is one (% by weight) determined by analysis of the NMR (nuclear magnetic resonance) spectrum of the resin obtained. The content shown in Table 3 is one (% by weight) calculated from the mixing ratio of the respective resins.

- 30 (2) Intrinsic viscosity 30  
The intrinsic viscosity is measured at 25°C in o-chlorophenol.

- (3) Melting point (softening point) and relative crystallinity  
The thermal behaviour was measured by a differential scanning calorimeter, Model DSC-1B, made by Perkin Elmer. The peak area due to melting is represented by a relative value, with the peak area of polytetramethylene terephthalate (Comparative Example in Table 1) being 100%. For non-crystalline resins, the softening point was measured by a micromelting point measuring apparatus made by Yanagimoto Shoji Co. Ltd. 35

- (4) Relative crystallinity  
The peak area observed when the resin is molten by the above-mentioned differential scanning calorimeter is measured, and a relative value of the peak value is calculated based on the supposition that the peak area of PBT (resin of Synthesis Example 1 in Table 1) is 100%. 40

- (5) Percent shrinkage  
A predetermined amount of the resin is compression-moulded at a temperature higher by 10°C than the melting point thereof in a mould having a length of 150 mm, a width of 25 mm and a thickness of 7 mm, and the moulded plate is allowed to stand still in a room maintained at a temperature of 23°C and a relative humidity of 50% for 48 hours and the change of the length (% based on the original length) of the moulded plate is determined. 45

- (6) Bending flexural modulus  
According to ASTM D-790, the bending flexural modulus was measured by using a Tensilon universal tester (Model UTM-III-500 supplied by Toyo Baldwin K.K.).  
It is added that the poly-2-methyl-1,3-propylene terephthalate content is based on the whole weight of the polyester resin. 50

#### Example 1

- 55 Into a reactor equipped with agitator blades of double helical ribbon type were charged 194.0 parts of dimethyl terephthalate, 121.5 parts of tetramethylene glycol, 13.5 parts of 2-methyl-1,3-propanediol, and 0.20 parts of titanium tetrabutoxide catalyst. The reactants were heated at 180°C for 1 hour under normal atmospheric pressure in a nitrogen stream and then heated at 230°C for 2.5 hours to distil off 94% of the theoretical quantity of methanol. After adding 0.02 parts of trimethyl 55

phosphate, the reaction products mixture was heated to 250°C and the system was evacuated to 0.2 mm H<sub>g</sub> over 40 minutes, and the reaction was carried out under this condition for 3.5 hours.

#### Example 2 and Comparative Example 1

Polymerization was carried out with the materials and amounts shown in Table 1 using the same procedures as in Example 1. Physical properties of the polymers obtained are shown in Table 1.

Table 1

	Items	Unit	Example 1	Example 2	Comparative Example 1	
10	Raw materials					
	Dimethyl terephthalate	Parts	194.0	194.0	194.0	10
	Tetramethylene glycol	Parts	121.5	87.7	135.0	
	2-Methyl-1,3-propanediol	Parts	13.5	47.3	—	
	Trimethyl phosphate	Parts	0.02	0.02	0.02	
	Tetrabutoxytitanium	Parts	0.20	0.20	0.20	
15	Poly-2-methyl-1,3-propylene terephthalate component	%	12	47	0	15
	Intrinsic viscosity	dl/g	0.80	0.83	0.82	
	Melting point	°C	213	141	229	
20	Relative crystallinity	%	77	8	100	20

#### Examples 3 to 6

Four kinds of polyester resins were prepared in the same way as in Example 1, except for the proportions of starting material as shown in Table 2, for the purpose of preparing the polymer blend according to the invention.

Table 2

			Example No.			
		Unit	3	4	5	6
Amounts Charged	dimethyl terephthalate	parts	194.0	194.0	194.0	194.0
	tetramethylene glycol	parts	135.0	121.5	87.7	—
	2-methyl-1,3-propane diol	parts	—	13.5	47.3	135.0
	trimethyl phosphate	parts	0.02	0.02	0.02	0.02
	tetrabutoxy titanium	parts	0.20	0.20	0.20	0.20
Content of poly-2-methyl-1,3-propylene terephthalate		%	0	12	47	100
Intrinsic Viscosity		dl/g	0.82	0.80	0.83	0.77
Melting Point		°C	229	213	141	105*
Relative Crystallinity		%	100	77	8	0

#### Note

\*: measured by a micro-melting point measuring apparatus supplied by Yanagimoto Shoji K.K.

#### Examples 7 to 9 and Comparative Examples 2 and 3

Polymer blends were prepared using respective polyesters as obtained in Examples 3 to 6 in the amounts shown in Table 3. Blending was effected by means of a Brabender mixer. The resulting blends were examined with respect to the percent shrinkage and blending flexural modulus.

Table 3

			Example No.			Comparative Example No.	
		Units	7	8	9	2	3
Mixed Amounts	Resin of Synthesis Example 3	parts	95	—	60	100	50
	Resin of Synthesis Example 4	parts	—	100	—	—	—
	Resin of Synthesis Example 5	parts	—	—	40	—	—
	Resin of Synthesis Example 6	parts	5	—	—	—	50
Content of poly-2-methyl-1,3-propylene diol		%	5	12	19	0	50
Percent Shrinkage		%	1.5	1.1	0.6	1.9	0.15
Bending Flexural Modulus		kg/mm <sup>2</sup>	240	220	190	260	160

### Claims

1. A polyester copolymer or polyester blend comprising tetramethylene terephthalate units and 2-methyl-1,3-propylene terephthalate units. 5
2. A polyester resin which comprises terephthalic acid units, tetramethylene glycol units and 2-methyl-1,3-propanediol units, the 2-methyl-1,3-propanediol units being contained in an amount of from 0.1 percent by weight, as 2-methyl-1,3-propanediol terephthalate, based on the whole weight of the polyester, to 99 mol percent, based on the total weight of the diol component. 10
3. A polyester resin as claimed in claim 2, wherein the polyester resin is a copolymer comprising terephthalic acid as the acid component and the as the diol component 1 to 99 mol % of tetramethylene glycol and 99 to 1 mol % of 2-methyl-1,3-propanediol. 15
4. A polyester resin as claimed in claim 3, wherein the diol component comprises 5 to 95 mol percent of 2-methyl-1,3-propanediol and 95 to 5 mol percent of tetramethylene glycol. 20
5. A polyester resin as claimed in claim 2, wherein the polyester resin is a copolymer which comprises 0.1 to 25 percent by weight, based on the whole weight of the polyester, of 2-methyl-1,3-propanediol terephthalate units. 25
6. A polyester resin as claimed in claim 5, wherein the copolymer comprises 1 to 20 percent by weight, based on the whole weight of the polyester of 2-methyl-1,3-propanediol terephthalate units. 30
7. A polyester resin as claimed in claim 2, wherein the polyester resin is a blend of polytetramethylene terephthalate resin and poly-2-methyl-1,3-propylene terephthalate and/or polytetramethylene-2-methyl-1,3-propylene terephthalate, the blend containing a 2-methyl-1,3-propylene terephthalate unit content of 0.1 to 25 weight percent. 35
8. A polyester resin as claimed in any of claims 1 to 7 which further comprises another monomer unit. 40
9. Polyester containing 2-methyl-1,3-propylene terephthalate units substantially as herein described with reference to and as illustrated in any of the Examples. 45

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